

VISCOELASTICITY OF COAL GEL FILMS PREPARED FROM SOLVENT-SOLUBLE CONSTITUENTS OF COALS

Toshimasa Takanohashi, Shigeki Isoda, Satoshi Doi, and Masashi Iino
Institute for Chemical Reaction Science, Tohoku University
Katahira, Aoba-ku, Sendai 980-77, JAPAN

KEYWORDS: Coal, Gel Film, Viscoelasticity

ABSTRACT

A large amount of solvent-soluble constituents of coals were mildly extracted with a carbon-disulfide - *N*-methyl-2-pyrrolidinone mixed solvent at room temperature. Various gel films containing a solvent was successfully prepared by using the solvent-soluble constituents and polar solvents such as *N*-Methyl-2-pyrrolidinone and *N,N*-dimethyl-formamide. A thermomechanical analysis (TMA) of the gel films was carried out and the creep compliance behaviors of the gel films showed the viscoelastic properties, suggesting that the gel films have mainly physical cross-linked networks through coal - coal interaction and coal - solvent interaction, since the solvent-soluble constituents have little original covalent cross-links. When the weight fraction of solvent in the gels was decreased, the viscous strain and the viscoelastic strain decreased, while the elastic strain was almost unchanged, suggesting no participation of a solvent. The network structure of homogeneous coal - solvent gel films and the coal - solvent interactions are discussed.

INTRODUCTION

Coal is considered to have cross-linked network structure consisting of various macromolecules, but the nature of network structure has not been well understood. Recently, it has been reported¹⁻³ that the network consists of physical cross-links through noncovalent interactions between coal molecules, not a covalently bound cross-linked network. The study on viscoelasticity of coal and coal-derived materials is one of the key to clarify cross-link structure of coal. To investigate the elasticity of coal network, coal thin sections were prepared and viscoelasticity of the pyridine swollen coal has been measured by Brenner⁴ and Cody et al.^{1,5} The pyridine swollen coals have been reported^{4,6} to show a rubbery elasticity. However, raw coal contains mineral matter and has a significant amount of pores and cracks on the surface, being liable to influence the measurement of elasticity of coals.

In our research groups, it has been found⁶⁻⁸ that by using a carbon disulfide - *N*-methyl-2-pyrrolidinone (CS₂-NMP) mixed solvent 40 wt % - 79 wt % of organic components in coals can be extracted at room temperature. The extract obtained is relatively homogeneous and has no ash.⁹ Since the extraction procedure includes no chemical reaction such as cleavage of covalent bonds in coals and addition reaction of the solvents with coals, the organic constituents originally existing in the raw coals are extracted.^{6,9} Recently, it has been succeeded¹⁰ to prepare gel films by mixing the homogeneous solvent-soluble constituents and polar solvent such as NMP or *N,N*-dimethyl-formamide at room temperature. In the present study, viscoelasticity of the gel films is measured and the network structure is discussed.

EXPERIMENTAL

Sample Preparation.

Upper Freeport coal (Argonne Premium Coal, 86.2 Cwt%) and Zao Zhuang coal (Shan Tong Province in China, 86.9 Cwt%) were used in this study. The coals (<150 μ m) were extracted with the mixed solvent under ultrasonication at room temperature. The two bituminous coals have been reported^{6,7} to give the high extraction yields with the CS₂-NMP mixed solvent, 59 wt% (daf), and 63 wt% (daf), respectively. The extract obtained was further fractionated with acetone and pyridine into acetone soluble (AS) fraction, acetone insoluble-pyridine soluble (PS) fraction and pyridine insoluble (PI) fraction under ultrasonication at room temperature. The PS and PI fractions were washed with acetone, while AS fraction was washed with acetone-water mixed solvent to remove the retained solvents. The extract fractions (AS, PS, PI) were dried under vacuum at 80 °C for 12 h. The fractionation procedure and the yields of each fraction of two coals are shown in Figure 1.

Gel Film Preparation.

Approximately 2 mL of solvent was added to 0.1 g of the coal extract fraction and was mixed under ultrasonication. After filtration with a membrane filter (0.8 μ m), the solution was placed in a glassware. The solvent in the solution was gradually removed under vacuum at room temperature. At some range of solvent wt % in the mixture, the

mixture became a lustrous gel film. By changing the evacuation time of solvent, the gel films containing different solvent composition (W_s) were prepared. The thickness of the films are the range of 50 μm – 200 μm .

Thermomechanical Analysis.

Viscoelasticity of the gel film was measured by a thermomechanical analysis apparatus (Shimadzu-TMA50). The small section of gel film was placed on the bottom plate. A load (stress) of 1 g was applied to the film section by using a detector bar, and a strain was measured from the decreased thickness of the film. Creep compliance measurements in which constant stress (5 g or 10 g load) was applied to the film, and stress-strain analyses in which the weight of load was changed were carried out.

RESULTS AND DISCUSSION

The Nature of Gel Film.

Figure 2 shows the weight fraction of NMP (W_s) in the Upper Freeport-PS fraction + NMP mixture (UFPS-NMP) when NMP was vaporized under vacuum. The W_s was decreasing with time by vaporization of NMP from the mixture and the slope became small around at $0.35 > W_s > 0.25$. In this range of W_s , it was observed that the mixture became lustrous gel film. For other fractions, PI, AI (PS+PI), the formation of similar gel films was observed, while for AS fraction which is a lighter fraction than the others, the mixture kept pasty even when W_s became little unchanged, i.e., no gel film formation. It has been reported that the AS fraction has lower average molecular weight and lower polar functional groups than other heavy fractions, suggesting that a physical cross-linked network by coal-solvent interaction and coal-coal interaction is important for the formation of gel films.

Creep measurements.

Figure 3 shows the creep compliance behaviors of three gel films with different W_s (0.70, 0.47, 0.30) which were obtained from UFPS-NMP mixture. The load of 5 g applied on the film was kept for 15 min, and then the load was released and the relaxation behavior was also measured. The procedure was repeated three times. In the case of $W_s=0.70$, the strain was greatly changed with an increase and a decrease in the load, showing the breaking of gel structure due to the stress. The strain is considered to be mainly due to viscous strain by the flow of solvent. On the other hand, for $W_s=0.47$ and 0.30, in the second and third scans, the reproducible data was obtained. Cody et al. analyzed² the creep compliance behavior of pyridine-swollen coal using a four-element Kelvin-Voigt model, which separates the strain into three strain elements, i.e., instantaneous elastic strain, ϵ_E , time-dependent viscoelastic strain, ϵ_{VE} , which decayed exponentially to a constant strain rate, and irreversible viscous strain ϵ_v , which was linear with time.

We also treated similarly. For the second and third scans for two gel films ($W_s=0.47$ and 0.30), total strain is represented as the following equation.

$$\epsilon(t) = \epsilon_E + \epsilon_{VE}(1 - \exp(-t/\tau)) + 100\sigma t/\eta \quad (1)$$

where t is time (s), τ is retardation time constant (s), σ is stress (Pa), and η is coefficient of viscosity (Pa s). In the eq. (1), the third term on the right describes viscous strain, $\epsilon_v(t)$. The calculated lines assuming ϵ_E , ϵ_{VE} , ϵ_v , τ and η in the eq. (1), for the second and third scans on the UFPS-NMP gel film ($W_s=0.30$) are shown in Figure 4. It was found that the calculated lines are well consistent with the experimental points for the both scans. A half of total strain is produced near $t=0$, i.e., instantaneous elastic strain. The strain at the second scan is more greatly increasing with time than that for the third one. The values of elastic strain, ϵ_E , viscoelastic strain, ϵ_{VE} , and coefficient of viscosity, η , are shown in Table I. For both samples, the changes of elastic strain, ϵ_E and viscoelastic strain, ϵ_{VE} were small between the second and the third scan, while coefficient of viscosity, η greatly increased, showing that the viscous strain is gradually decreasing. In $W_s=0.30$, the viscoelastic strain and the viscous strain were small, while the elastic strain was a little large, compared to the case in $W_s=0.47$, suggesting that the elastic strain may originate from physical cross-links through noncovalent interactions between macromolecules in the heavy extract fraction, as well as relatively strong interactions between coal macromolecules and the solvent.

Stress-Strain Curve.

A load was increased from initial 1 g to 10 g at a constant rate, 1 g/min, and then the load was decreased at the same rate. The procedure was repeated several times. The stress-strain curves of UFPS-NMP gel films with $W_s=0.53$ and 0.30, are shown in Figure 5 and 6,

respectively. Figure 5 shows that the first and the second scan gave a large strain. The first large strain is considered to be attributed to the structural changes by the viscous strain. While after the forth scan a similar stress-strain curve was obtained, suggesting that the structural changes of gel becomes reversible with repeating the increase and decrease in the stress. Figure 6 shows that the strain change is small compared to that for $W_s = 0.53$ shown in Figure 5. This result suggests that the gel film is more elastic, since the amount of the solvent is small and relatively strong interactions must have still remained in the gel film, resulting in the large contribution of the elastic component.

CONCLUSIONS

Homogeneous gel films containing no mineral matter could be prepared from the mixture of the solvent-soluble constituents with polar solvents such as *N*-methyl-2-pyrrolidinone and *N,N*-dimethyl-formamide. It is suggested that the gel films have physical cross-linked networks through coal-coal interaction and coal-solvent interaction, since the solvent-soluble constituents themselves have little extended covalent cross-links. When the weight fraction of solvent in the gels was decreased, the viscous strain and the viscoelastic strain decreased, while the elastic strain was almost unchanged. It was found that a similar stress-strain curve is obtained after several cycles of the increase and decrease in the stress, indicating that a constant structural change with changing the stress occurs.

ACKNOWLEDGMENT

This work has been carried out as one of "Research for the Future" project of the Japan Society for the Promotion of Science (JSPS) through the 148 committee on coal utilization technology of JSPS.

REFERENCES

1. Cody, G. D. J.; Davis, A.; Hatcher, P. G. *Energy Fuels* **1993**, *7*, 463.
2. Fujiwara, M.; Ohsuga, H.; Takanohashi, T.; Iino, M. *Energy Fuels* **1992**, *6*, 859.
3. Takanohashi, T.; Iino, M.; Nishioka, M. *Energy Fuels* **1995**, *9*, 788.
4. Brenner, D. *Fuel* **1985**, *64*, 167.
5. Cody, G. D. J.; Davis, A.; Hatcher, P. G. *Energy Fuels* **1993**, *7*, 455.
6. Iino, M.; Takanohashi, T.; Ohsuga, H.; Toda, K. *Fuel* **1988**, *67*, 1639.
7. Takanohashi, T.; Iino, M.; *Energy Fuels* **1990**, *4*, 452.
8. Iino, M.; Takanohashi, T.; Ohkawa, T.; Yanagida, T. *Fuel* **1991**, *70*, 1236.
9. Iino, M.; Takanohashi, T.; Obara, S.; Tsueta, H.; Sanokawa Y. *Fuel* **1989**, *68*, 1588.
10. Iino, M.; Watanabe, H.; Takanohashi, T. *Inter. Conf. Coal Sci.*, Oviedo, **1995**, vol. 1, p.59.

Table 1 The Values of Elastic Strain(ϵ_E), Viscoelastic Strain(ϵ_{EV}), and Viscosity (η)

	$W_s = 0.30$		$W_s = 0.47$	
	second	third	second	third
ϵ_E (%)	0.55	0.53	0.47	0.43
ϵ_{EV} (%)	0.08	0.06	0.13	0.13
$\eta \times 10^{10}$ (Pa s)	11.3	19.0	5.0	8.5

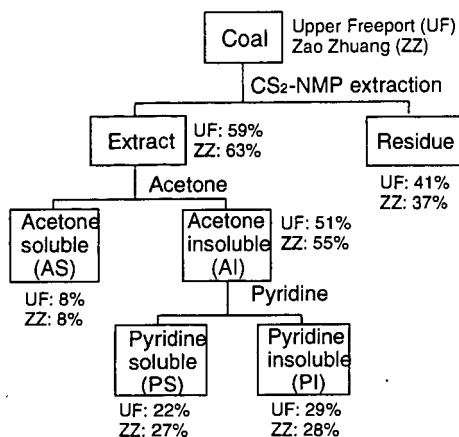


Fig.1 Extraction and Fractionation Procedures

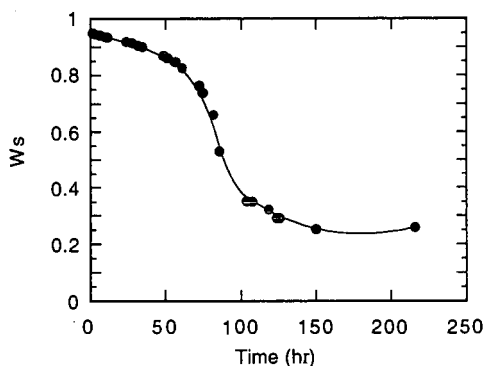


Fig.2 Weight Fraction Change of UFPS+NMP under vacuum at room temperature

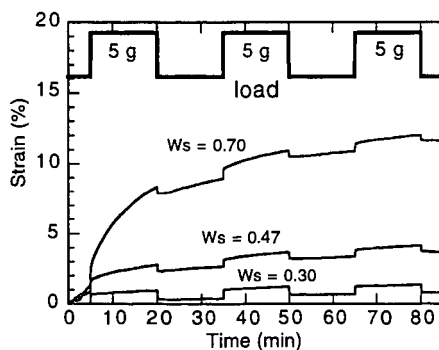


Fig.3 Creep Compliance of UF-PS - NMP gel: (Ws = 0.30, 0.47, 0.70)

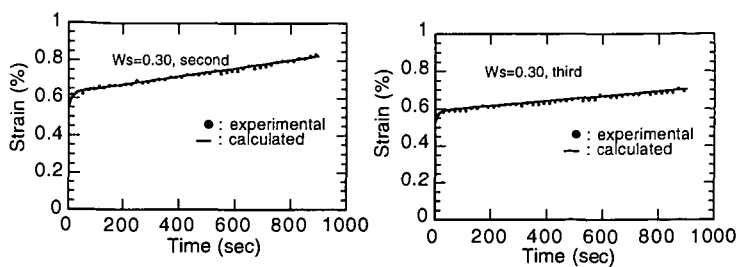


Fig.4 The Fitting Curves for the Second Scan (a) and the Third Scan (b) of Creep Compliance of UFPS - NMP Gel ($W_s = 0.30$)

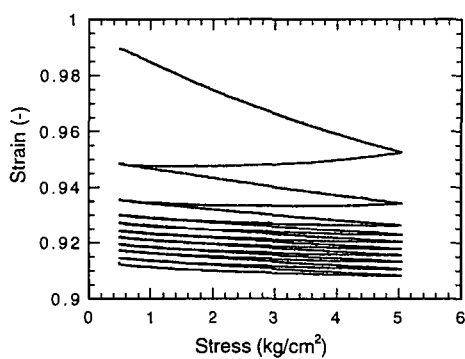


Fig. 5 The Stress-Strain Curve of UFPS - NMP Gel Film ($W_s=0.53$)

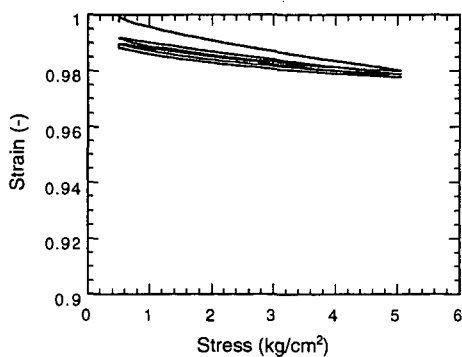


Fig.6 The Stress-Strain Curve of UFPS - NMP Gel Film ($W_s=0.30$)